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POLYCHLORINATED DIBENZO-P-DIOXINS, DIBENZOFURANS, AND BIPHENYLS IN FREGATA MAGNIFICENS FROM ILHA GRANDE BAY, RIO DE JANEIRO STATE, SOUTH-EASTERN BRAZIL

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ABSTRACT

The purpose of this paper is to perform analyses in a fish-eating seabird species which is recognized to be at risk of accumulating toxic contaminants due to its high position in the trophic web and to its low ability to metabolize xenobiotic compounds. *Fregata magnificens* were collected at Ilha Grande Bay, Rio de Janeiro, Brazil (23°8’26"S, 44°14’50"W) between February, 2009 and April, 2013. Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs), were analyzed in tissue composites, being subsequently identified and quantified using gas chromatography coupled with mass spectrometry. The concentrations were below the range of concern established by World Health Organization. The sum of PCB-congeners analyzed had the concentration of 968 pg/g lipid weight, and 13.9 pg TEQ/g lipid weight. The PCDD/F-congeners analyzed had the concentration of 331.04 pg/g lipid weight, and 13.4 pg TEQ/g lipid weight. This type of study aims to integrate information from analyses of seabirds with halogenated hydrocarbons and could also make contribution to the scientific support for political decisions on coastal zone management.

RESUMO

O objetivo deste trabalho é realizar análises químicas em tecidos da ave marinha *Fregata magnificens* que se alimenta de peixes. Esta ave é reconhecida por estar em risco de acumular contaminantes tóxicos, devido a sua alta posição na teia trófica e a sua baixa capacidade de metabolizar compostos xenobióticos. Exemplares de *Fregata magnificens* foram coletados na Baía da Ilha Grande, Rio de Janeiro, Brasil (23°8’26"S, 44°14’50"W) entre fevereiro de 2009 e abril de 2013. Concentrações de dibenzeno-p-dioxinas policloradas (PCDD), dibenzofuranos policlorados (PCDF) e bifenilas policloradas (PCBs) foram analisadas em compostos de tecido, sendo posteriormente identificados e quantificados por cromatografia gasosa acoplada à espectrometria de massas. Os resultados indicam que as concentrações estavam abaixo do limite de segurança estabelecido pela Organização Mundial de Saúde. A soma dos congêneres de PCBs analisados apresentou a concentração de 968 pg/g de peso lipídico e 13,9 pg TEQ/g de peso lipídico. Os congêneres de PCDD/Fs analisados tiveram a concentração de 331,04 pg/g de peso lipídico e 13,4 pg TEQ/g de peso lipídico. Este tipo de estudo tem por objetivo integrar informações de análise de aves marinhas com hidrocarbonetos halogenados e, também, pode contribuir dando apoio científico para as decisões políticas sobre gestão da zona costeira.

Descriptors: Ilha Grande Bay, Halogenated hydrocarbons, *Fregata magnificens*, Contamination, Anthropic actions, Sustainability.
Descritores: Baía da Ilha Grande, Hidrocarbonetos halogenados, *Fregata magnificens*, Contaminação, Ações antrópicas, Sustentabilidade.

INTRODUCTION

Halogenated aromatic compounds, typified by the polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs), are industrial compounds or by-products which have been widely identified in the environment and in chemical-waste dumpsites (LAUWERYS; HOET, 1993). Halogenated aromatics are invariably present in diverse analyses as highly complex mixtures of isomers and congeners, complicating a secure detection and risk assessment of these compounds

(SAFE, 1990). They persist in the environment (XU et al., 2013) in target bioaccumulation in living organisms, often preferentially in the lipid or fatty tissues (TANABE et al., 2004; PARERA et al., 2013).

Due to the strength of the carbon-chlorine bond there is a tendency to be more resistant to the common degradation pathways in the environment and organisms, which causes them to have an environmental half-life of several years to even decades (DORNELES et al., 2013), increasing the concentration throughout the food chain, in such a way as to cause toxic effects, especially at the highest trophic levels (MORIARTY, 1999; KUMAR et al., 2002).This longevity enables them to be transported over long distances either through the atmosphere or by ocean currents, depending on the physical properties of the molecule (ALCOCK et al., 1998). Many of these compounds have been deliberately produced as agricultural pesticides (e.g. DDT (Dichlorodiphenyltrichloroethane), Chlordane (Hexachlorocyclopentadiene) and Lindane (gamma-hexachlorocyclohexane)) or for use in industrial applications (e.g. PCBs and Brominated Flame retardants), while others were or are still being produced as by-products of industrial synthesis or incomplete combustion (e.g. PCDDs) (ALLEN et al., 2008). Even today, some of them are still deliberately used. For instance, DDT can still be used for Malaria control in Africa (RANSON et al., 2011), and is still used as an anti-fouling agent in paints in China (LIN et al., 2009). This leads to an estimated environmental release of 250 tons per year (UNEP, 2007). The increasing use of chemical waste and agricultural drainage systems represents the most dangerous chemical pollution (GARCÍA DE LA PARRA et al., 2012). Knowledge of the oceans and the impact of human activities on them can reveal the complexity and interdependence of all the aspects of the system (FERREIRA, 2008). Improved acquaintance with the oceans and improved predictive capabilities are required for more effective and sustained development of the marine environment to obtain associated economic benefits and to preserve marine resources (COSTANZA; FARLEY, 2007; GORNI; WEBER, 2004).

The marine environment receives organochlorine compounds through wet and dry deposition at the water-surface, and by diffusive vapour exchange between air and water (WANIA et al., 1998). Transport of these compounds from sediment to water is of great concern since it is suspected that historically polluted sediments may act as a source to the overlying water column, and thereby prolong the exposure of biota, long after emissions have been stopped. The key processes that determine their transport across the sediment-water interface are: (a) the sedimentation and resuspension of particles, (b) the diffusive movement of the organochlorine compounds and also when attached to dissolved organic matter (HOLMSTRÖM; BERGER, 2008).

In ecosystems, organisms interact through complex trophic relationships, which involve energy and nutrient flow between trophic levels. Understanding trophic relationships, as well as quantitatively assessing trophic levels is of fundamental importance for the comprehension of ecosystem structure. Seabirds are good indicators of productivity and health in the marine environment (TASKER; REID, 1997; PARRISH; ZADOR, 2003). Their patterns of distribution and abundance are strongly correlated with primary production (WHITEHOUSE et al., 1999), with the abundance of fish shoals (FREDERIKSEN et al., 2008) and nest-site availability (FASOLA; CANOVA, 1992; BOURGEOIS et al., 2008). Population fluctuations, mass mortality and other anomalies in their populations can be taken as criteria indicating the presence of contaminants in the sea (KUSHLAN, 1993) and abrupt amendments to climate change (JENOUVRIER et al., 2003, STEMPNIEWICZ et al., 2007). Worldwide, seabird research has undergone a major evolution in terms of data collection, interpretation of information and application in the field of management and policy (TASKER; REID, 1997). Seabirds have, thus, been used in several environmental monitoring studies (LAUWERYS; HOET, 1993; CHOY et al., 2010).

Magnificent Frigatebirds *Fregata magnificens* occur along the tropical and subtropical coasts of the Americas (HARRISON, 1983). Colonies of the species are widely distributed in Brazil, being found in Fernando de Noronha, Bahia, Rio de Janeiro, São Paulo, Paraná and Santa Catarina (COELHO et al., 1991; ALVES; VECCHI, 2009). The detailed knowledge of general seabird ecology and of the numbers and productivity of many populations also makes them particularly appropriate as bioindicators. This knowledge has several benefits, e.g. the large quantities of data collected from a particular site can be separated in a relatively short period of time. *F. magnificens* as a fish-eating bird is well suited for the assessment of the effects of PCDD/Fs and PCBs due to its wide distribution. Additionally, it is particularly appropriate as a biomonitors of pollutants whose concentration is increased along the food chain (ALVES; VECCHI, 2009).

The present study sought to evaluate the concentrations of PCDD/Fs and PCBs in *F. magnificens* (Ilha Grande Bay, Rio de Janeiro, Brazil) that breed on the South Atlantic Ocean, where local pollution by PCDD/Fs and PCBs is presumed to be negligible or non-existent.

Material and Methods

Study Site

The Ilha Grande Bay is a large area located in Rio de Janeiro state, Brazil. It is characterized by a system of estuarine and oligotrophic waters, with a significant diversity of marine ecosystems, such as rocky shores, islands, mangrove forests and sandy beaches (Fig. 1). The weather is hot, tropical and humid, with average annual temperature of 22.5°C, and water temperature varying between 18°C and 24°C. The region is relatively well preserved, still presenting vestiges of the insular Atlantic Forest, and is considered a priority area for conservation. It has great scenic beauty, a rich fauna and flora, and is therefore a natural sanctuary for biodiversity (a hot-spot), and lies between the two largest cities in South America - the cities of Rio de Janeiro and São Paulo. This richness and diversity of species, still little known, are due to geographical peculiarities, and its being a hydrographic oceanographic region, coupled with factors such as the diversity and connectivity of coastal systems, input of organic matter from rivers, physical variation and chemical oceanographic factors (ALHO et al., 2002).

The area of Ilha Grande Bay is home to the territories of the cities of Parati and Angra dos Reis, which together had 145,000 inhabitants in 2010. In view of the beautiful landscape of the region, its main vocation naturally focuses on tourism and nautical leisure activities. Consequently, along the coast there is a series of developments that, through the occupation of hillsides, riverbanks or islands and the landfilling of mangrove areas, cause deforestation and polluted coastal waters. This growth as a tourist hub has promoted haphazard development and caused severe damage to the coastal systems. There are still other large projects planned for the region, such as a commercial port, a petroleum terminal, an iron-ore terminal, two nuclear power plants and a shipyard. This area was selected for this study because of the large number of the birds harbour that inhabit it (NUNES; SANTOS, 2012).

Sample Collection and Handling

Dead or injured *F. magnificens* adults were collected from the Ilha Grande Bay (23°8’26"S, 44°14’50"W). Samples were collected between February, 2009 and April, 2013. After collection the birds were examined externally and necropsied in accordance with a standardized protocol (JAUNIAUX et al., 1998). Livers were collected, weighed and kept frozen until analysis.

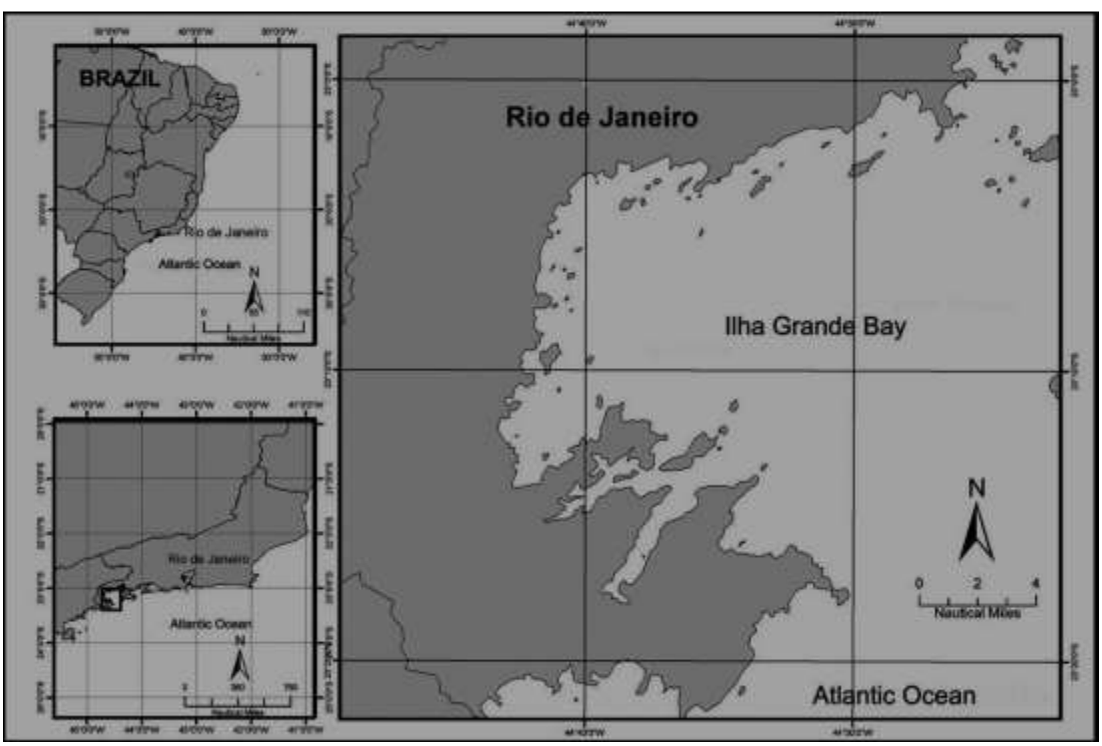

Fig. 1. Map of the study area: Ilha Grande Bay, Rio de Janeiro State, South-eastern Brazil.

Analysis of Dioxin, Furan, and PCB Congeners

The analytical procedures were undertaken in accordance with previous reports (KUMAR et al., 2001; SHAW et al., 2006; PARVEZ et al., 2013). Moisture content was determined and samples were extracted using a Soxhlet apparatus for 10-15 hours in dichloromethane. Briefly, after the extraction, samples were concentrated to 10 ml using a Kuderna-Danish (K-D) concentrator and the solvent transferred to n-hexane. Lipid content was determined gravimetrically from an aliquot of the extract. Seventeen 13C-labeled 2,3,7,8-substituted tetra-, penta-, hexa-, hepta-, and octa-CDD and CDF congeners and twelve dioxin-like PCBs (IUPAC Nos. 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189) were spiked into hexane extracts prior to sulphuric acid treatment. The hexane layer was rinsed twice with hexane-washed water, and dried by passing through anhydrous sodium sulphate in a glass funnel. The solution was concentrated to 2 ml and sequentially subjected to silica gel, alumina and silica gel-impregnated activated carbon column chromatography. Extracts were passed through activated silica gel packed in a glass column (Wakogel, silica gel 60; 2 g) and eluted with 130 ml of hexane, which contained PCDD/DFs and dioxin-like PCBs. The hexane extract was K-D concentrated and passed through activated alumina column (Merck-Alumina oxide, activity grade 1; 5g) and eluted with 30 ml of 2% dichloromethane in hexane as the first fraction, which contained several *ortho*-substituted PCBs. The second fraction eluted with 30 ml of 50% dichloromethane in hexane contained PCDD/DFs and dioxin-like PCBs, which was purged under a gentle stream of nitrogen to 0.5 ml and passed through a silica gel impregnated activated carbon column (0.5 g) to further separate mono- and di-*ortho* PCBs from non-*ortho* PCBs and PCDD/DFs. The first fraction eluted with 25 ml of 25% dichloromethane in hexane contained mono and di-*ortho* PCBs. The second fraction eluted with 250 ml toluene contained non-ortho PCBs and PCDD/DFs. Sample extracts were analyzed by a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). Procedural blanks (n=3) were analyzed to check for interferences. PhD and HpCDF were detected in blanks at concentrations approximately <0.01 pg/g, and OCDD at approximately 0.1 pg/g. The values obtained for HpCDD, OCDD and HpCDF were not corrected for the blank concentrations.

Identification and Quantification

Identification and quantification of 2378-substituted congeners of PCDD/DFs and dioxin-like PCBs were performed by use of a (i) Shimadzu GC-14B gas chromatograph with AOC-1400 auto-sampler. Columns: CBP-1 (SE-30) and CBP-5 (SE-52/54 confirmatory column). Injection: Splitless (30 seconds) 300°C. Temperature program of the oven: 110°C (1 minute); 15°C/min up to 170°C; 7.5°C/min up to 290°C, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector (63Ni) temperature: 310oC; (ii) HPLC: Shimadzu LC-10AS; Mobile phase: acetonitrile: water 80%, isocratic run. Column: Shimadzu STR-ODS-II (C18 reverse phase) 25cm, L: 4mm ID. UV/VIS detector model: Shimadzu SPD-10A. Prior to injection, 13C-labeled 1234-TeCDD and 123789-HxCDD were added as injection recovery standard. Mean recovery of spiked internal standard through the whole analytical procedure was 74% (range: 60–95%) and the reported concentrations were not corrected for the surrogate recoveries. PCDD/DFs, dioxin-like PCBs and TEQ concentrations are reported on a lipid weight basis using WHO TEF for birds (VAN DEN BERG et al., 2006) as pg TEQ/g, lipid weight.

Statistical Tests

The hypothesis of normal distribution (Shapiro-Wilk's W test) was not rejected for log-transformed data. Lipid base log-transformed concentrations were used to determine the significant differences between group geometric means (Tukey test). Null hypothesis (equality of means) was rejected at the 95% significance level ($p<0.05$).

Results

PCDD, PCDF, and PCB Congeners

Results for the congener-specific analysis of PCDD, PCDF, and PCB congeners are given in Table 1 and **2**. 2,3,7,8-Substituted PCDD and PCDF congeners were detected in all samples analyzed (n=17). No significant sex-related differences in PCDD/F or PCB concentrations were found. Fat-based log-transformed concentrations were used to determine whether there were significant differences between group geometric means. Null hypothesis (equality of means) was rejected at the 95% significance level ($p<0.05$).

There were no statistically significant differences between mean PCDD/F and PCB-congeners concentrations. The five most abundant congeners were 2,3,4,7,8-pentachlorodibenzofuran (PeCDF) > 1,2,3,7,8- pentachlorodibenzo-*p*-dioxin (PeCDD) > 1,2,3,7,8-pentachlorodibenzofuran (PeCDF) > 1,2,3,7,8,9 hexachlorodibenzo-*p*-dioxin (HxCDD) > 2,3,4,6,7,8-hexachlorodibenzofuran (HxCDF). Polychlorinated biphenyl congeners were detected in all samples analyzed. The sum of the 12 congeners analyzed had the concentration of 968 pg/g lipid weight, and 13.9 pg TEQ/g lipid weight. The sum of 17 congeners analyzed of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans had the concentration of 331.04 pg/g lipid weight, and 13.4 pg TEQ/g lipid weight.

Toxic equivalents, calculated using TEFs for birds proposed by WHO (VAN DEN BERG et al., 2006), and compositions are shown in Figure 2. Correspondingly, from a toxicological point of view, even if the TEF values for these minor contaminants were as high as those of PCBs, or even of PCDDs, the contribution to TEQs would be small compared to those of PCDDs, PCDFs, and PCBs.

Table 1. Medians (range) of PCDD/Fs (pg/g, lipid weight) and toxic equivalents of PCDD/Fs (pg TEQ/g, lipid weight) concentrations in *Fregata magnificens.*

Elements	*Fregata magnificens*	
	Concentration	**WHO TEF (birds)**
Dibenzo-p-dioxins (PCDD)		
2378-TCDD	0.6 (0.2 - 4)	0.6
12378-PeCDD	3 (0.5 - 8)	3
123478-HxCDD	14 (6 - 44)	0.7
123678-HxCDD	5 (1 - 9)	0.05
123789-HxCDD	9 (5 - 31)	0.9
1234678-HpCDD	35 (6 - 66)	0.035
OCDD	199 (33 - 291)	0.0199
2378-TCDF	0.34 (1 - 4)	0.34
12378-PeCDF	16 (9 - 31)	1.6
23478-PeCDF	4.9 (2 - 32)	4.9
123478-HxCDF	8.2 (2 - 32)	0.82
123678-HxCDF	3 (1 - 12)	0.3
1234789-HxCDF	7 (1– 30)	0.7
234678-HxCDF	3 (2 - 12)	0.3
1234678-HpCDF	9 (3 - 23)	0.09
1234789-HpCDF	5 (2 - 22)	0.05
OCDF	9 (2 - 19)	0.0009
	Σ= 331.04	Σ= 13.4

Table 2. Medians (range) of PCBs (pg/g, lipid weight) and toxic equivalents of PCBs (pg TEQ/g lipid weight) concentrations in *Fregata magnificens.*

Elements	*Fregata magnificens*	
	Concentration	**WHO TEF (birds)**
Non-ortho PCBs		
3,3’,4,4’-TCB (77)	86 (33 - 543)	4.3
3,4,4’,5-TCB (81)	47 (18 - 550)	4.7
3,3’,4,4’,5-PeCB (126)	48 (32 - 111)	4.8
3,3’,4,4’,5,5’-HxCB (169)	67 (26 - 104)	0.067
Mono-ortho PCBs		
2,3,3’,4,4’-PeCB (105)	244 (37 - 289)	0.0244
2,3,4,4’,5-PeCB (114)	185 (55 - 312)	0.0185
2,3’,4,4’,5-PeCB (118)	134 (49 - 244)	0.00134
2’,3,4,4’,5-PeCB (123)	61 (22 - 114)	0.00061
2,3,3’,4,4’,5-HxCB (156)	18 (7 -72)	0.0018
2,3,3’,4,4’,5’-HxCB (157)	24 (4 - 33)	0.0024
2,3’,4,4’,5,5’-HxCB (167)	35 (13 - 53)	0.00035
2,3,3’,4,4’,5,5’-HeCB (189)	19 (7 - 29)	0.00019
	Σ= 968	Σ= 13.9

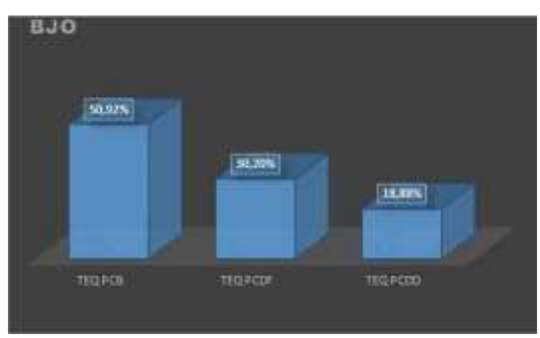

Fig. 2. Contributions of PCDDs, PCDFs and dioxin-like PCBs to total TEQ.

DISCUSSION

The success of modern societies is, in part, based on extensive achievements in chemistry with a systematic, resulting development of products in medicine, agriculture, and in almost all manufacturing industry sectors and materials for daily use. Chemistry, thus, contributes to the quality of life of billions of human beings. However, its negative impacts on the environment and on health are an important issue of public concern. Social and ecological concerns should not be disregarded in spite of the economic interests affected.

Increased human activities such as industrialization, coupled with over-population and increased atmospheric temperatures, among other factors, have become major environmental issues in recent years. As a result of such circumstances, additional studies which include these environmental factors and their indicators are important because they can show the potential impacts that result from them and their effects on public health. Thus the study of ecotoxicology, a very broad field of science in which issues such as uptake by and effects on organisms, as well as distribution and residence time of the pollutants in the trophic level are studied in many different ways, is of growing importance.

Data on contaminant levels in Brazilian seabirds are limited, and no information exists regarding levels of new or emerging contaminants. High concentrations of PCDD/F and PCB congeners have been shown to adversely affect the reproductive capacity of birds (CUSTER et al., 2010). The adverse effects observed range from direct toxic and teratogenic effects on developing embryos (YAMASHITA et al., 1993; HARRIS et al., 2005) to subtle changes in parental behaviour (HARRIS et al., 2005). A comprehensive example of these effects has been the study of reproductive effects in fish-eating waterbirds in the northern Baltic (HARIO et al., 2004).

The fundamental question to answer is whether the trophic level is harmfully disturbed when polluted by toxicants. To answer this important question, quantitative understanding of the pollutants behaviour within ecosystems is essential, and therefore researchers develop methods to manage this. The presence of anthropogenic pollutants, such as PCDD/F and PCB-congeners, throughout all compartments of the marine environment has been of international concern for a number of decades (KUMAR et al., 2002). While a great number of datasets documenting absolute concentrations of persistent organic pollutants in a variety of marine biota are available, the bioaccumulative nature, toxicity, biomagnification, and the fate of these compounds in the marine ecosystem is still poorly understood.

The predominant compounds have been PCBs that have presented 98.15 ng/g in *F. magnificens*. Contrasting also with data obtained from significant concentrations of PCBs which have been detected in all oil samples, with a concentration ranging from 9 - 4834 ng/g lipid and a geometric mean of 404 ng/g lipid (YAMASHITA et al., 2007), and by higher concentrations of PCBs which had been reported in tissues of seabirds that feed near industrialized areas (e.g., near North America) than in those that feed in remote areas (e.g., Bering Sea) (TANABE et al., 2004), the low levels of contaminants suggest a relative degree of isolation and preservation, but the occurrence and distribution profiles of PCBs support the hypothesis that the main source of contamination in remote areas is long range atmospheric transport, and demonstrate the ubiquity of those pollutants in the marine environment.

In previous studies, the monitoring of POPs in seabirds has been limited by the availability of organs (SHAFFER et al., 2006). This approach can easily be combined with ecological investigations of seabirds, and so this could dramatically increase the availability of seabird samples, including repeated sampling of identical birds (HOLMSTRÖM; BERGER, 2008). Recently, electronic tracking tags have revolutionized our understanding of the large-scale movements and habitat use of mobile marine animals (SHAFFER et al., 2006). LAILSON-BRITO et al. (2010), studying organochlorine accumulation in Guiana dolphin (*Sotalia guianensis*), at the same study site found concentration levels from 765 to 99 175 for ΣPCB.

Although the data presented in this study are not a cause for concern, subsequent analyses involving more environmental and faunal aspects are necessary. The current study is the first to report seabirds' concentrations of PCDD/Fs and PCBs at this study site, and the first for any free-ranging birds from the Ilha Grande Bay. Due to the small size of the population studied, continued monitoring of these pollutants is essential for the assessment of the health and viability of these animals. Biomagnification may be the cause of the levels in the species collected and analyzed. Further assessments are recommended of organisms at higher trophic levels to assess ecotoxicological impacts. The ubiquity of these pollutants in the marine environment of Ilha Grande Bay supports the need for a greater awareness of bioaccumulation processes, particularly for organisms cultivated (shellfish) or fished locally and destined for human consumption.

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